Docket No. 10621-3

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

5   Applicant: Clarke et al

Serial No.   09/976,987   Group Art Unit: 1772

Filing Date: Oct. 12, 2001   Examiner Rhee, Jane J

Title: Gas-permeable Membrane

10   Assistant Commissioner for Patents

Washington, DC 20231

DECLARATION

15   I, Raymond Clarke, declare as follows.

1.   I am a coinventor of the invention described in the above-identified application,
which I shall refer to in this declaration as "the present invention" and "the present
application" respectively. I am also a coinventor of U.S. Patent Nos. 5,412,035 and
20   6,210,724, and U.S. Patent No. 6,376,032, which issued on the parent application of
this application. I am employed by Landec Corp., the assignee of the present
application and of United States Patents noted above. I have more than eight years
experience in the use of coated microporous films to modify the atmosphere within
packages containing respiring materials. In this declaration (as in the present
25   application), I shall refer to oxygen permeability by the abbreviation OTR, and to the
ratio of carbon dioxide permeability to oxygen permeability by the abbreviation R ratio.

2.   The following facts were known before the present invention was made.
        (A)   A microporous film has a very high OTR and an R ratio of 1.
30   (B)   A uniform polymeric film has (1) an R ratio which depends on the chemical
        composition of the polymer, and is greater than 1, and (2) an OTR which is much

less than the OTR of a microporous film and which depends on the chemical composition of the polymer and the thickness of film.

(C)   A gas-permeable membrane comprising (a) a microporous film and (b) a polymeric coating on the film, can be used as an atmosphere control member to modify the atmosphere within a package containing respiring materials. The permeability of the membrane is preferably high enough for the control member to be of convenient dimensions. For packaging some, but not all, respiring materials, it is desirable that the coated film should have a high R ratio, for example at least 3 or at least 4.

3.   The present application discloses for the first time a number of valuable discoveries about the use of gas-permeable membranes comprising a microporous film and a polymeric coating on the film. One of those developments is that, as explained in detail in the present application, improved results are obtained when few or no large pores are present in the microporous film. The present application also discloses that microporous films having desired pore size characteristics can be prepared by the extraction process described in U.S. Patent Nos. 4,937,115 and 3,351,495.

4.   I have carefully reviewed United States Patent No. 5,160,768, which I shall refer to in this declaration as "Antoon". Antoon discloses the use of certain coated microporous films as atmosphere control members (Antoon refers to them as "panels") to provide a controlled atmosphere within a container. Antoon notes

(a)   that the coated membrane should have a "permeability sufficient to allow the type of control required within a reasonable time and an area suitable for the amount of produce being packaged" (column 4, lines 25-47), and

(b)   that the carbon dioxide/oxygen permeance ratio (i.e. the R ratio) is preferably 4 to 5 (column 5, lines 13-16).

5.   Although Antoon refers to microporous films in general, the only microporous films specifically disclosed are those made by the process described in column 4, line 48, to column 5, line 16. That process involves casting a sheet of a mixture of a

polymer and a filler (preferably a mixture of polypropylene and calcium carbonate), and drawing the sheet under orienting conditions, so that the polymer pulls away from filler, causing the formation of voids and pores in the polymer matrix. Antoon states that the degree of permeability resulting from this process depends on the amount of filler, the

5   amount of draw and the temperature at which the drawing is carried out.

6.   I have been informed that paragraph 3 of the outstanding Office Action contains the following statement.

It is the Examiner's position that the gas-permeable membrane of U.S. Patent

10   *5,160,768 is identical to or only slightly different than the gas-permeable membrane prepared by the method of the claim(s), because both gas-permeable membranes have a microporous polymeric film and a polymeric coating on the microporous film, and both have an oxygen permeance of at least 775,000 ml/m^2 .atm.24hrs (50,000 cc/100 in^2.atm.24 hrs) and a CO_2 /O_2 permeability ratio*

15   *(R) of least 1.5.*

It appears to me that this statement is based upon an incorrect assumption, namely that because each of two gas-permeable membranes has an OTR and an R ratio above a certain minimum, they are identical or only slightly different from each other. The OTR and R ratio of a gas-permeable membrane can vary widely above the stated minimum

20   values, and this variation can result from the use of microporous films and/or polymeric coatings which differ from each other. Even when two gas-permeable membranes have substantially the same OTR and R ratio, they can be based on substantially different microporous films and/or substantially different polymeric coatings. Even when the polymeric coating is the same, gas-permeable membranes based on different

25   microporous films can have OTR and R values which are greater than the stated minimum values, but which are widely different from each other.

7.   I have been informed that paragraph 4 of the outstanding Office Action contains the following statement.

30   *Since Antoon teaches a microporous membrane having the recited permeability and CO_2 /O_2 permeance ratio for use in preserving produce, as disclosed by the*

> *applicant, it would have been obvious to one of ordinary skill in the art to have provided the recited pore size and density in the microporous film.*

It appears to me that this statement is based upon an incorrect assumption, namely that one of ordinary skill in the art, knowing nothing of the present application, understood the relationship between the "pore size and density" of a microporous film and the 0TR and R ratio of a gas-permeable membrane made by coating the microporous film with a polymer. As noted above, I believe that the present application is the first disclosure of that relationship, in particular the fact that improved results are obtained when few or no large pores are present in the microporous film. I do not think that there is anything in Antoon which suggests that the microporous film should have the pore size characteristics set out in the claims of the present application. Indeed, the opposite is true. Column 3, lines 30-34, of Antoon states

> *A critical feature for high permeance and high $CO_2 : O_2$ ratio... is that the substrate film, although often much thicker than the coating, should be at least two times (preferably at least 10 times) as permeable as the coating itself.*

Since larger pores lead to higher permeability, this passage does not suggest that larger pores should be avoided, but rather that their presence is desirable.

8.   In the invention claimed in Claim 1 of the present application, the voids in the microporous film are produced by an extraction process. The extraction process is carried out on a sheet which is produced by melt processing a mixture of a polymer, a processing oil and a filler. The sheet is treated with an organic extraction liquid to extract the processing oil, and then the extraction liquid remaining in the polymeric sheet is removed by steam or water. Further information about such extraction processes can be found in U.S. Patent Nos. 4,937,115 and 3,351,495, both of which are referred to in the present application.

9.   The drawing process used by Antoon to prepare his microporous films is clearly different from the extraction process defined in Claim 1 of the present application. Furthermore, the different processes produce microporous films which are quite different from each other.

In Antoon's process, the voids are produced by sudden violent rupture of the solid polymeric matrix. The rupture is triggered at points of weakness created by the filler, and the voids are produced in an essentially random fashion until the drawing

5 forces have been accommodated. By contrast, in the extraction process, the polymeric matrix remains substantially unchanged, and the voids have substantially the same shapes as the pockets and channels of the processing oil before the oil is removed by the extraction; and those shapes are dependent on the viscosities and surface tensions of the polymer matrix and the processing oil during the melt processing step. The voids

10 remaining after the extraction are, therefore, quite different from those produced by Antoon's drawing process.

10.   The differences between Antoon's drawing process and the extraction process are reflected in their different pore size characteristics. Antoon's process results in

15 microporous sheets which are less consistent in their pore sizes, have a wider range of pore sizes and have a greater proportion of larger pores. As a result, coated membranes based on Antoon's microporous sheets are inferior to those based on microporous sheets prepared by the extraction process or which have pore size characteristics similar to sheets prepared by the extraction process. As noted in the

20 present application, it appears that the reason for this is that the larger pores are not blocked (or not completely blocked) by the coating polymer, especially at the low coating weights which are preferred in order to obtain adequate oxygen permeability. As a result, the permeability characteristics of the coated membrane insufficiently reflect the properties of the coating polymer.

25

11.   Antoon contains six specific Examples of coated membranes. In Examples 1, 2, 3, 5 and 6, the microporous films (films A, B, C, E and F in Table 3) are films made by drawing a sheet composed of polypropylene and calcium carbonate, the drawing being biaxial except in Example 3 (Film C) in which it is uniaxial. In Example 4, the

30 microporous film (film D in Table 3) is a commercial microporous polypropylene film sold by Enka under the tradename Accurel 2E HF. Accurel 2E HF is no longer commercially

available, but the attached Data Sheet provides some information about it, in particular that it has a nominal pore size of 0.2 micron and a maximum pore size of less than or equal to 0.8 micron. Examples 7-10 are comparative examples.

5   12.   Antoon does not report the pore size characteristics of his microporous films. However, the results in Antoon's specific Examples make it clear that his coated products do indeed suffer from the disadvantages that result from a wide range of pore sizes and the presence of substantial proportions of relatively large pores.

10   Table A below sets out, for each of Examples 1-6, the OTR, R ratio and polymer coating weight of the coated membrane, arranged in descending order of coating weight. I have calculated the coating weights from the information given in Antoon's Table 3. In Example 1, 0.3034 grams of Dow Corning 734 are spread over a 3.5" diameter circle, resulting in a coating weight of 0.032 g/in^2. The coating weights in
15   Examples 2-4 are similarly calculated. In Example 5, 0.255 grams of an emulsion are applied twice. The polymers in 80 parts of the emulsion are 15 parts of the silicone and 2 parts of the polyvinyl alcohol (10% of 20 parts of the Vinol product), resulting in a total of 0.255 x 2 x 17/80 (= 0.11) grams of polymer applied to a 3.5" diameter circle, i.e. a coating weight of 0.011g/in^2. Similarly, in Example 6, assuming that the "less than 0.1
20   gram" of emulsion is in fact 0.09 gram, the coating weight is 0.004 g/in^2.

Table A

Antoon Example #	1	2	3	5	6	4
Coating weight g/in^2 (g/m^2)	0.032 (4.96)	0.027 (4.18)	0.026 (4.03)	0.021 (3.25)	0.011 (1.71)	0.004 (0.62)
OTR cc/100 in^2.atm.24 hrs (in thousands)	19	25.2	9.2	24.3	54.1	226.8
R	3.5	3.4	3.5	4.1	3.0	3.5

Table B below sets out the coating weight (expressed as the percentage of the
25   coating polymer in the coating composition), OTR and R ratio values for Examples 2D,

2E, 2F and 2G of the present application. In those Examples, the microporous film is Teslin SP7, which is produced by the extraction process (as noted on the paragraph beginning on page 7, line 24 and ending on page 8, line 5, of the present application, as amended by the Preliminary Amendment filed with the present application) and which

5   has the pore size characteristics set out on page 17, lines 22-23 of the present application. As noted on page 16, line 6 of the present application, the "Sil" in those Examples is Silastic 734 from Dow Corning, which I believe to be the same material as the "Dow Corning 734" silicone elastomer used in Antoon's Examples.

Table B

Application Example #	2G	2F	2E	2D
Percentage Silastic 734 in coating	100	50	40	35
OTR cc/100 in^2.atm.24 hrs (in thousands)	25	52	64	104
R	5.3	4.7	4.1	3.0

10

Comparison of Tables A and B demonstrates the advantages of using a microporous film prepared by the extraction process and/or having the pore size characteristics resulting from the extraction process. Table A makes it clear that, when the microporous film has been prepared by the drawing process, neither the OTR nor

15 · the R ratio of the coated membranes is a function of the coating weight. Table B, by contrast, makes it clear that, when the microporous film has been prepared by the extraction process and/or has the resulting pore size characteristics, there is a progressive reduction in the R ratio of the coated membrane, and a progressive increase in its OTR value, as the coating weight of the Silastic 734 is reduced.

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It is also to be noted that, when the microporous film has been prepared by the drawing process, it is not possible, even at relatively high coating weights, to obtain a coated membrane having an R ratio which fully reflects the R ratio of the coating polymer. As is shown by the R ratio of 5.3 in Example 2G of Table B, the R ratio of Dow

25   Corning 734, on its own, is at least 5.3. Yet the highest R ratio achieved by Antoon is

4.1 (in Example 5), and the remaining Examples have R ratios of 3.5 or less. This is in spite of fact that Antoon states that the R ratio is preferably 4 to 5.

13.   The drawing process described in Antoon is also described in U.S. Patent No. 4,879,078, in which the inventor (Antoon) and the assignee (Hercules Inc.) are the same as in Antoon. U.S. Patent No. 4,879,078 was filed about seven months before Antoon. It discloses the use, as an atmosphere control member, of a microporous film made by the uniaxial drawing process stated to be preferred in Antoon. In each of the Examples of U.S. Patent No. 4,879,078 (as in each of the examples of Antoon) the film is composed of polypropylene with calcium carbonate dispersed therein).

So far as I know, it is not now possible to purchase microporous film made by the drawing process described in Antoon. I have, however, obtained a product which is a microporous film and which I believe to be a microporous film made by Antoon's drawing process. I obtained this product from Apio Inc., which is a subsidiary of Landec Corp. Apio Inc., some years ago, purchased a company called Fresh King Inc. The product, which I shall refer to as the Fresh King product, was part of the assets acquired by Apio Inc. from Fresh King Inc. The Fresh King product is a microporous film which has no polymeric coating on it, but which does have printing on it. I have had the Fresh King product analyzed to determine its components, and the analysis showed that the microporous film is composed of polypropylene with calcium carbonate dispersed therein. I believe that the microporous film was supplied to Fresh King Inc. by Hercules Inc. (the assignee of Antoon) and that Fresh King applied printing to the film, with the intention of using the printed film as an atmosphere control member in the packaging of melons and strawberries, in the way described generally in U.S. Patent No. 4,879,078.

I have had the Fresh King product subjected to mercury porosimetry to determine its pore size characteristics, and Table C below sets out the pore size characteristics in relation to the various limitations present in claims 20-23 of the present application.

Table C

	Claim 20	Fresh King
Average Pore Size (micron)	< 0.24	0.132
% pores < 0.24 micron	> 70%	82 %
% pores < 0.014 micron	< 20%	22%
% pores < 0.15 micron	> 80%	57%
	Claim 21	
% pores < 0.24 micron	> 90%	82 %
	Claim 22	
% pores < 0.24 micron	100%	82%
	Claim 23	
% pores < 0.11 micron	> 70%	40%

Table C makes it clear that the Fresh King product, although it has an average pore size less than the permitted maximum of 0.24 micron, has many more pores whose size is greater than 0.15 micron than is permitted by the definition in Claim 20. Similarly, the Fresh King product contains too many relatively large pores to meet the requirements of claims 21-23

The undersigned, having been warned that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001, and that such willful false statements may jeopardize the validity of the present application and any patent granted thereon, declares that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true.

Dated *December 2 nd* , 2002

Raymond Clarke.

Raymond Clarke

Data Sheet

ACCUREL® PP
Flat Membrane

TYPE				2E HF-PP			Test Spec. No.
Pore size	nominal			0.2		µm	708/711
	maximum		≤	0.8			
Bubble point (N_2 against IPA)	minimum		≥	0.76	bar		
Retention of bacteria pseudomonas diminuta		log. reduction value	≥	8			780/0.701
Transmembrane flow at 25 °C	IPA		≥	8.5	$\frac{ml}{cm^2 \cdot min \cdot bar}$		708/709
	nitrogen		≥	2.8	$\frac{l}{cm^2 \cdot min \cdot bar}$		708/710
Standard width				300 ± 10	mm		
Thickness				140 – 180	µm		708/715
Burst pressure			>	0.85	bar		708/714
Tensile strength	dry	longitudinal	>	350	cN/15 mm		708/712
		transversal	>	450			
Elongation at break	dry	longitudinal	>	30	%		
		transversal	>	40			
Change of length at 121 °C (steam)		longitudinal	≤	3	%		708/713
		transversal	≤	2			
Extractables (pore forming agent)			≤	0.1	%		780/701

The information contained in this data sheet reflects the company's knowledge and experience at the time of issue. No guarantee can, however, be given as to its completeness. Neither must it be construed to embody any liability on the part of Enka over and above that assumed under the company's "General Conditions of Sale" for membranes, section VI and VII.

A certificate on the composition of ACCUREL® PP (= Polypropylene) Flat Membrane can be provided on request. The material meets the requirements of USP XXI, Class VI.

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